# Achieving Optimum Throughput in ICP-MS Analysis of Environmental Samples with the Agilent 7500ce ICP-MS

Application

**Environmental**


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## Abstract

**Throughput enhancements in ICP-MS can be achieved by minimizing sample uptake and rinse-out time through various techniques as well as by reducing data acquisition time. Depending on the application and data quality objectives, significant reductions in average run-to-run time are possible. In this work, we present some practical tips as to how to optimize several areas within the conventional ICP-MS sample introduction and data acquisition systems and make use of new rinse modes within the new Agilent ChemStation to improve productivity. The new methodology is supported by application to the analysis of the entire suite of 21 EPA method 200.8 elements plus 5 mineral elements and internal standards in a mixed run of drinking waters, leachates, and high-matrix wastewaters in approximately 4.5 minutes.**


## Introduction

High throughput in ICP-MS depends not only on accurate, high-speed data acquisition, but on rapid and complete sample wash-in and wash-out. In fact, as instrument scan speed and data processing speed have improved, it is sample wash-in/wash-out that remains the main limiting factor in achieving minimum run-to-run times and best detection limits, especially for memory-prone elements like Hg, Ag, Sb, Mo, and Tl. Complex, discrete sampling or flow injection techniques have successfully reduced sample uptake and rinse-out times to very low levels. However, until now, little systematic work has been done to efficiently optimize the conventional ICP-MS sample introduction system for highest possible throughput.

The topic of this application note is the maximization of sample throughput through:

- Understanding uptake and rinse out
- Optimization of the conventional sample introduction system on the Agilent 7500 Series ICP-MS for maximum productivity
- Minimization of acquisition time
- Use of intelligent software functions that eliminate wasted time in sample uptake and rinse out

## Understanding Uptake and Rinse Out

In theory, minimizing the time it takes to get the sample into and out of the ICP-MS involves only two simple principles, one physical and one chemical.

First, minimize the time required for the sample to flow to the nebulizer. This can be done by minimizing the volume of the flow path and/or maximizing the flow while avoiding mixing at the interface between subsequent samples/blanks as much as possible. At the same time, it is desirable to minimize higher than optimum sample flow to the nebulizer itself to reduce plasma and interface overloading.

Second, minimize chemical interactions such as adsorption/desorption of soluble components in the sample to the sample introduction system. This is especially critical for the analysis of Hg, which must frequently be measured at ultra-trace levels and is very memory prone. These can be addressed by controlling the solution chemistry, sample introduction materials, and the contact surface area and exposure time.

## Optimizing the Plumbing

Optimizing the plumbing involves minimizing the total volume of the sample introduction system, including the autosampler probe, peristaltic pump tubing, and sample transfer tubing. The internal diameters of these components should also be minimized in order to reduce the total wetted surface area. The mixing tee where the internal standard and sample are mixed is relocated to the top of the peristaltic pump in order to shorten the distance to the nebulizer as much as possible. The “tails” are clipped from the sample peristaltic pump tubing, leaving only about 1 cm beyond the stops, significantly reducing both the volume and surface area. Of all the polymer components used in the sample introduction system, polyvinyl chloride (PVC), used for the peristaltic pump tubing, is the most prone to causing carryover. Therefore, in order to further reduce the volume and surface area, smaller diameter peripump tubing can be used. In this case, the pump speed must be increased accordingly to maintain proper nebulizer flow. Pump speed correction factors are shown in Table 1. To convert from the standard 1-mm internal diameter (ID) tubing to a smaller size, multiply the normal pump speed used with the 1-mm tubing by the factor shown to maintain the same flow. Switching from 1-mm tubing to 0.64-mm tubing can reduce the sample rinse-out time by as much as 50%.

**Table 1. Correction Factors for Various Internal Diameter Peristaltic Pump Tubes Used to Maintain Correct Nebulizer Flow**

| Peristaltic pump tubing ID (mm) | Correction factor |
|---|---|
| 0.89 | 1.3 |
| 0.76 | 1.8 |
| 0.64 | 2.55 |

## Minimization of Data Acquisition Time

Significant improvements in ICP-MS quadrupole, detector, and electronic technology have resulted in much better sensitivity and precision than earlier instruments. As a result, shorter integration times can be used while detection limit performance can be maintained or even improved. Total acquisition time is also reduced in Agilent ICP-MS instruments through the use of intelligent, variable quadrupole settling time, which reduces time between mass jumps. In the case of collision/reaction cell instruments such as the Agilent 7500ce or 7500cs, minimization of stabilization time during cell mode switching is also critical. Agilent’s Octopole Reaction System (ORS) features a very small-volume cell that minimizes the time needed for gas switching and stabilization. Typically, 15 seconds is sufficient to achieve stable conditions after gas switching.

## New Intelligent Software Capabilities (Revision B.03.03)

The ChemStation’s new software features have been designed to eliminate wasted time in both sample uptake and rinse out, significantly reducing run times without compromising data quality. Customers with earlier revisions can upgrade to the newest B.03.03 revision by contacting their Agilent sales or service representative.

### Pre-emptive Rinse

Pre-emptive Rinse utilizes the volume of the sample introduction tubing (autosampler probe,

sample tubing, and peristaltic pump tubing) to maintain sample flow to the nebulizer *after* the autosampler probe has moved to the rinse position and begun rinsing. On conventional ICP-MS systems, the autosampler probe moves to the rinse position only after acquisition has finished; as much as 30 to 60 seconds can be wasted with the probe sitting in the sample vial waiting for the acquisition to finish. With Pre-emptive Rinse enabled, the autosampler probe moves from the sample to the rinse port at a preset time *before* acquisition has finished, using the sample still in the uptake tubing for the remaining data acquisition. This provides two benefits:

1. No time is wasted while sample flushes from the sample introduction system after acquisition has finished.
2. When the peristaltic pump speed is increased to rinse after a sample, it is pumping rinse solution, not the previous sample. This significantly reduces the total matrix load on the interface since only rinse solution and not sample is introduced at a high rinse flow rate. As a result, interface maintenance is reduced and stability is enhanced.

#### Intelligent Rinse

Intelligent Rinse is designed to ensure that the absolute minimum amount of time is spent washing out each sample — *independent* of analyte concentration. On systems without Intelligent Rinse, the fixed, postsample rinse time must be long enough to wash out the highest anticipated analyte concentrations, and the most memory-prone analytes, to blank levels. This means that for back-to-back samples of similar concentration or very clean samples, unnecessary time is wasted in rinsing. Intelligent Rinse monitors the background level of up to 10 user-selected elements (or element ratios) to determine when sufficient rinsing has occurred. Since Intelligent Rinse supports internal standard correction (or any other count ratio), it is not necessary to update the background thresholds if the instrument sensitivity changes. Only Agilent Intelligent Rinse provides this level of sophistication. Intelligent Rinse supports up to three distinct rinse steps (for different rinse solutions) in addition to the probe rinse port on the autosampler. Each of these rinse steps can be controlled with respect to rinse time and uptake speed. Any of these rinse steps, including the probe rinse port, can be selected as the Intelligent Rinse step. When using Intelligent Rinse, in many cases, background levels are achieved immediately and the rinse terminates after only a few seconds.

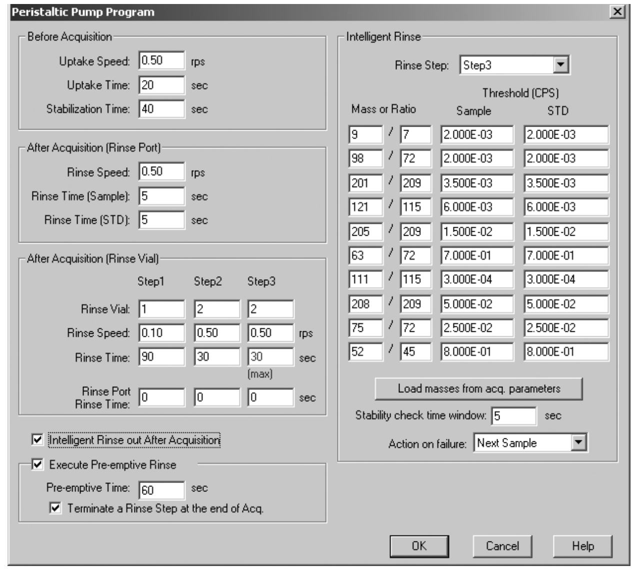


**Figure 1. Peristaltic pump program setup panel showing typical settings for both Intelligent and Pre-emptive Rinse functions.**

The result is that the shortest possible rinse times that allow complete washout are always achieved. The peristaltic pump control panel that is used to configure Intelligent Rinse is shown in Figure 1.

## Putting It All Together

By combining optimized plumbing, Pre-emptive and Intelligent Rinse functions, and streamlined data acquisition parameters, typical average run-to-run times for complex environmental samples — including sticky elements such as Hg — can be reduced by almost 50%.

## Rinse Program

The rinse program is shown in Figure 1. Pre-emptive Rinse time is set to 60 seconds, which immediately reduces the run time by a minute and reduces matrix loading on the plasma and interface. By the time the acquisition is finished, the rinse solution (Step 1 in this case) has nearly reached the nebulizer and most of the system is already rinsed. Between each rinse step, a small bubble is introduced into the line, helping to partition the solutions and minimize mixing. Step 2 is the main rinse and the only step using high-speed rinse out. Step 2 is set to 30 seconds, though much shorter times are often sufficient. Step 3 is the Intelligent Rinse step, which is functionally a monitor step. This means that the system will only rinse in Step 3 until the specified background elements reach the set points, or up to a maximum of 30 seconds in this case. At that point, rinsing is

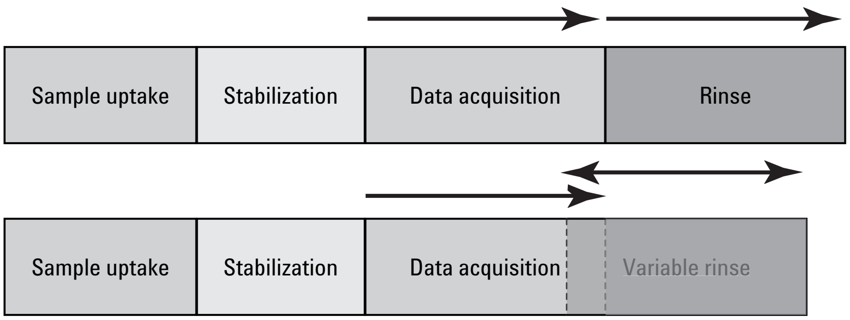


**Figure 2.** Graphical representation of sample analysis time using conventional uptake and rinse program (top) versus uptake and rinse utilizing Pre-emptive Rinse and Intelligent Rinse (bottom).

**Table 2.** Comparison of Total Sample Introduced Under Typical Conditions Using Normal Rinse Program Versus Pre-Emptive Rinse. Up to 20% Less Sample Is Introduced Using Pre-Emptive Rinse

| | Standard mode | Pre-emptive rinse |
|---|---|---|
| Sample uptake | 1.2 mL/min * 20 sec = 0.4 mL | 1.2 mL/min * 20 sec = 0.4 mL |
| Stabilization | 0.4 mL/min * 30 sec = 0.2 mL | 0.4 mL/min * 20 sec = 0.13 mL |
| Sample analysis | 0.4 mL/min * 180 sec = 1.2 mL | 0.4 mL/min * 180 sec = 1.2 mL |
| Rinse out | 1.2 mL/min * 15 sec = 0.3 mL | 0 |
| **Total sample** | **2.1 mL** | **1.73 mL** |

finished and the next sample is introduced. Figure 2 is a graphical representation of the different ways in which Pre-emptive Rinse and Intelligent Rinse reduce sample analysis time.

## Streamlined Data Acquisition

Table 3 depicts the additional time savings by optimizing the acquisition integration times, taking into account the high sensitivity provided by the 7500ce[1]. In this case, the entire suite of 21 EPA method 200.8 elements (including Hg, plus the five mineral elements (Na, Mg, K, Ca, and Fe), plus internal standards were analyzed using optimized cell conditions (three modes — $H_2$, He, and no gas) in 4.5 minutes average sample-to-sample time. Excellent (ppt level) method detection limits (MDLs) were achieved. Carryover, as indicated by the analysis of a blank solution run immediately after a 100 ppb (10,000 ppb for the mineral elements) standard was extremely low. When data quality objectives permit, switching to a single ORS mode (either no gas or He only) can reduce the average analysis time to less than 3 minutes.

[1]Acquisition parameters of 1 point per peak were used, with integration times per point from 0.1 to 0.5 seconds depending on the element and ORS mode.

**Table 3.** Typical Data Showing Blank Concentration Directly After a 100/10,000 ppb Standard and Calculated Method Detection Limits (3 Sigma) from 10 Separate Replicate Analyses of a 0.1 ppb Standard

1 point/peak acquisition
Average analysis time – 4.5 mins

| Sample | Cal 100.0/10000 (ppb) | Blank (ppb) | MDL (ppb) |
|---|---|---|---|
| Be/9 [#3] | 99.89 | 0.020 | 0.0205 |
| Na/23 [#2] | 9987 | 0.088 | 4.6245 |
| Mg/24 [#2] | 9946 | 1.419 | 1.7648 |
| Al/27 [#3] | 99.61 | –0.028 | 0.0239 |
| K/39 [#2] | 9951 | 0.573 | 2.0353 |
| Ca/40 [#1] | 10020 | 2.387 | 1.9820 |
| V/51 [#2] | 99.98 | –0.010 | 0.0193 |
| Cr/52 [#2] | 99.69 | 0.003 | 0.0156 |
| Mn/55 [#2] | 99.69 | 0.015 | 0.0258 |
| Fe/56 [#1] | 9986 | 2.731 | 0.6361 |
| Co/59 [#2] | 99.63 | 0.013 | 0.0092 |
| Ni/60 [#2] | 99.43 | 0.015 | 0.0100 |
| Cu/63 [#2] | 99.26 | 0.012 | 0.0292 |
| Zn/66 [#2] | 99.59 | –0.020 | 0.0288 |
| As/75 [#2] | 100 | 0.003 | 0.0286 |
| Se/78 [#1] | 99.77 | 0.019 | 0.0299 |
| Mo/95 [#3] | 101.8 | 0.018 | 0.0219 |
| Ag/107 [#3] | 99.32 | 0.021 | 0.0085 |
| Cd/111 [#3] | 99.97 | 0.012 | 0.0167 |
| Sb/121 [#3] | 100.7 | 0.026 | 0.0168 |
| Ba/137 [#3] | 99.92 | 0.009 | 0.0256 |
| Hg/201 [#3] | 2.012 | 0.004 | 0.0048 |
| Tl/205 [#3] | 100.3 | 0.021 | 0.0089 |
| Pb/208 [#3] | 100.5 | 0.012 | 0.0127 |
| Th/232 [#3] | 100.8 | 0.020 | 0.0104 |
| U/238 [#3] | 101.1 | 0.015 | 0.0084 |

#1 — $H_2$
#2 — He
#3 — no gas

## Conclusions

### Faster Sample Runs, Higher Confidence

Sensitivity is maintained, maintenance is reduced, confidence in results is improved, and valuable time is never wasted. Pre-emptive Rinse reduces the total sample-to-sample pre-emptive time by at least 60 seconds, while also exposing the system to less total sample matrix (Table 2). More importantly, the sample matrix is never delivered to the nebulizer at high flow rates, thereby significantly increasing the number of samples that can be run between maintenance intervals.

Intelligent Rinse ensures that, after very clean samples, the rinse thresholds will be met immediately and almost no time will be spent in the final rinse solution, eliminating most of the 30- to 60-second available time. Furthermore, Intelligent Rinse can be counted on to rinse as long as necessary (up to a user-defined limit), ensuring that adequate rinsing will always occur. Rinse time will always be as long as necessary and never any longer. Additionally, the user has the choice of determining which elements need the most complete rinse out. Critical elements, like Hg, that require very low detection limits and are very memory-prone can be analyzed with confidence at ppt levels, even in unknown samples, while the washout threshold of high-level mineral elements such as Na can be set at a much higher level, or ignored if desired.

An illustration of high productivity made possible by the new Agilent ChemStation rinse modes is given by the following example: A 7500ce ORS instrument, analyzing a mixed run of drinking waters, leachates, and high-matrix wastewaters, operating in three modes ($H_2$, He, and no-gas), covering a full environmental analyte suite including the mineral elements and Hg, has an average sample-to-sample analysis time of 4.5 minutes — without any risk of carryover from unexpectedly high samples.

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